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Synthesis and optical characterization of CdS nanocomposites

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Abstract Nanocrystalline films are deposited in plastic substrates and particles in powder form are prepared by precipitation method from the same colloidal solution The size and distribution of the crystallites are controlled by varying the temperature of the bath solution from 28°C to 90°C The crystallite sizes are determined from X ray diffraction and are found to be around 7 nm in films and 15 – 10 nm in powder The band gaps are determined from the UV absorption spectra and are found to be within the range from 2 48 2 75eV in films and 2 48 2 64 eV in powder Photoluminescence measurements shows enhancement of PL intensity for films at higher temperatures whereas excitonic emission at 376 nm and red shift around 603 nm is observed for precipitates

Keywords Chemical method nanomaterial UV spectra photoluminescence energy band gap

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1. Introduction

Semiconductor nanocomposites like all nanomaterials are found to exhibit properties different from those of the same materials in bulk form[1,2] Evidences of variations of the properties with sizes of the particles open up new theoretical, experimental and technological interests Of the II-VI semiconductors CdS have received wide attention because of its immense application potentials in optoelectronic nanodevices[3,4] CdS is a typical direct band gap semiconductor having band gap of 2 42 eV for bulk material which increases when crystallite size decreases Sizes of the CdS clusters depend strongly upon their preparation conditions and methods[5,6,7] The simple way of synthesizing CdS nanoclusters is through an arrested precipitation reaction of Cd^{2+} and S^{2} in an aqueous solution with the presence of a stabilizing agent, such as polymers[8], zeolites[9], or porous glass[10].Out of several methods for deposition of nanocomposites, chemical bath

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deposition (CBD) technique using polymer matrix is relatively simple, cost effective and suitable for deposition of large area films.

2. Experimental details

In the present work systematic analysis on the growth of the film by CBD technique as well as on homogeneous precipitation of clusters taking place simultaneously in the solution are carried out.The deposition was carried out in a mixture of matrix solution and thiourea

The matrix solution was prepared by adding cadmium sulphate to an aqueous solution (2%) of polyvinyl alchohol (PVA) with constant stirring at constant temperature (70°C) maintained for 90 minutes. Different solutions were prepared with the same concentration of cadmium sulphate (1M) The pH of the solutions were maintained at around 11, by slowly adding NH_4OH solution. Then the equimolar solutions of thiourea were added to the mixture solutions kept at different temperatures (28°C & 90°C). Deposition of CdS thin film at higher temperature facilitates comparatively faster growth of the film Plastic substrates were introduced vertically into the solution with the help of substrate holder The substrates were kept in the solution for 20 hrs at room temperature and 20mins at elevated temperatures for deposition of films. After deposition the substrates were taken out and thoroughly washed and rinsed with doubly distilled water and dried in air The CdS precipitate that formed in the bath was filtered out and after thoroughly washing by distilled water was allowed to dry for two days in a desiccator containing silica gel at room temperature.

2 1 Characterization of CdS thin films :

All the measurements were done at room temperature. Grain sizes of the films and precipitates were measured by X-ray diffractometer (Philips X-pert Pro diffractometer (PW 1830)) with CuK_α radiation in the 2θ range of $20^\circ - 35^\circ$ Surface morphological study were done using the Scanning Electron Microscope (SEM) (LEO 1430 VP) operating with an accelerating voltage 20 kV. Optical absorption spectra at 300 K were obtained using a UV visible spectrophotometer (VARIAN CARY 300 Scan) in the wave length range 300 nm to 700 nm. Photoluminescence (PL) spectra were obtained with a luminescence spectrometer(Thermo Spectronic(Aminco Bowman Series 2)) operating at detector voltage 700 volt with an excitation light wavelength of 325 nm.

3. Results and discussion

3.1. X-ray diffraction :

The X-ray diffractogram of the CdS nanocrystalline films and precipitates show broadened diffraction profiles (Figure 1(a) and (b)). It is observed that XRD patterns show a preferred orientation along (002) plane.The observed XRD pattern exhibits hexagonal phase as confirms from JCPDS data 08-006.The crystallite sizes of the nanocrystallites are estimated using Scherrer formula

$$D = K\lambda/\beta_{2\theta}\cos\theta \qquad (1)$$

where K is a constant taken to be 0.94, λ the wave length of X-ray used (λ =1.54A°) and $\beta_{2\theta}$ the full width at half maximum of (002) peak of XRD pattern, Bragg angle 2θ is around 26.5°. The crystallite sizes were found to be about 7 nm for films, and 15 -10

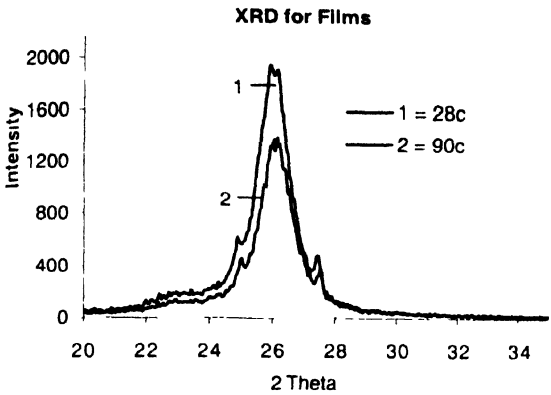

Figure 1 (a). XRD patterns for films deposited at temperatures 28°C and 90°C.

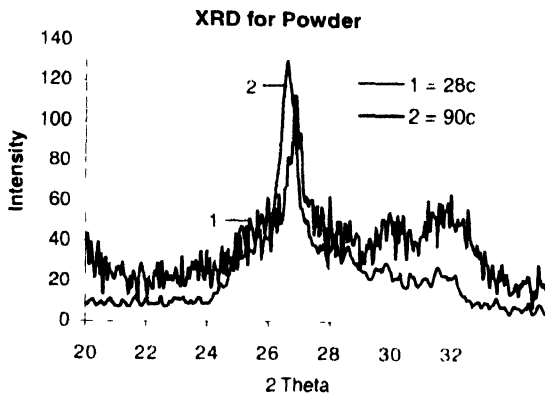

Figure 1 (b). XRD patterns for precipitates deposited at temperatures 28°C and 90°C

nm for precipitates and are shown in Table 1. It is observed that crystallite size decreases with the increase in temperature of the solutions.

Table 1. Crystallite sizes and band gaps for CdS nanocrystalline films and precipitates having different temperatures

Sl.No.	Temp of the soln's (°C)	Grain Size (nm) From XRD	Grain Size (nm) From SEM	Band Gap (eV) From UV spectra
Film 1	28	7	47-54	2 48
Film 2	90	7	32-37	2 75
Powder 1	28	15	82-94	2 48
Powder 2	90	10	59-74	2 64

3.2. SEM analysis :

Figure 2(a) and (b) show the surface morphology of the CdS nanocomposites deposited at two different temperatures observed by SEM. From the Figure, we clearly observe the small nanosized grains engaged in a fibrous-like structure, which clearly indicates the nanocrystalline nature along with some amorphous phase of CdS thin films. From these images, it can be seen that the grain sizes are not uniform and found to be about 32 – 94 nm and shown in Table 1.

3.3. Absorption studies :

The UV absorption spectra of the CdS thin films and of the precipitates obtained from different solution temperatures (28°C and 90°C) are taken at room temperature and shown

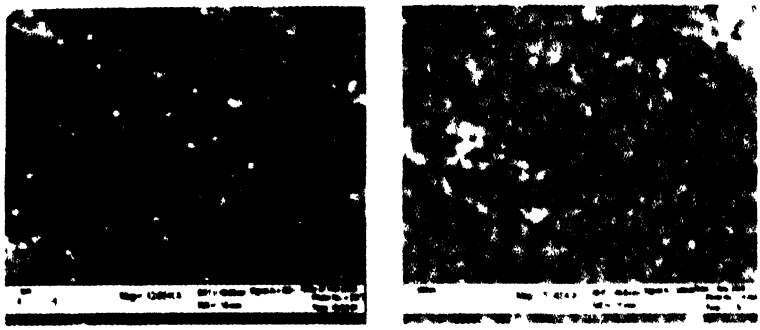

Figure 2(a). SEM pictures for films at temp 28°C and 90°C

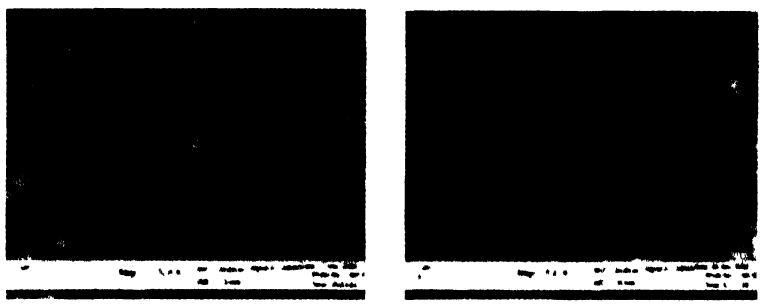

Figure 2(b). SEM pictures for precipitates at temp 28°C and 90°C

in Figure 3(a) and (b) From the spectrographs the absorption edge of the samples are found to occur in the range 340-490 nm.

Absorption spectrum shows a clear shift of the absorption edge to the lower wavelength side over bulk value at ~ 515 nm. This blue shift of the absorption edge indicates decrease of the crystallite sizes of the samples. The absorption coefficient is given by

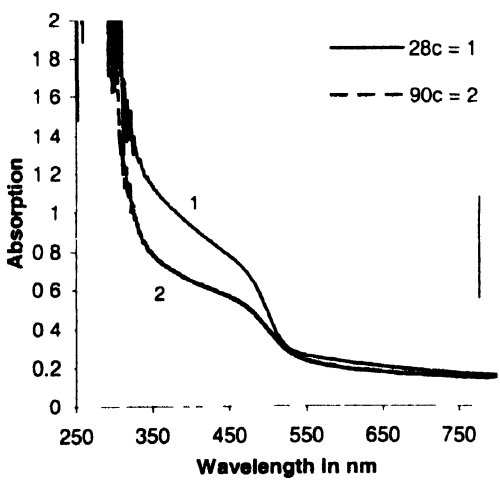

Figure 3(a). UV spectra for films at temp 28°C & 90°C

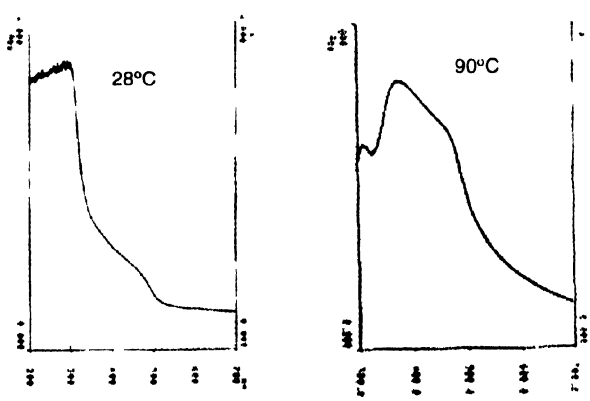

Figure 3(b). UV spectra for precipitates at temp 28°C & 90°C

$$\alpha = c\left(h\nu - E_g\right)^{1/2} / h\nu, \tag{2}$$

where α is the absorption coefficient, c is a constant, $h\nu$ the photon energy and E_g the band gap. A graph between $h\nu$ vs $(\alpha h\nu)^2$ is plotted and shown in Figure 4(a) and (b). The extrapolation of straight line to $(\alpha h\nu)^2 = 0$ axis gives the value of the energy band gap of the materials and the band gaps are found to be within 2.48 – 2.75 eV. The band gap increases with the decrease of crystallite sizes.

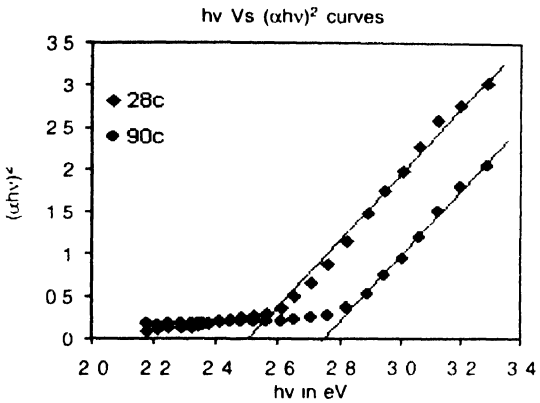

Figure 4(a) Band gap determination for films at temp. 28°C & 90°C.

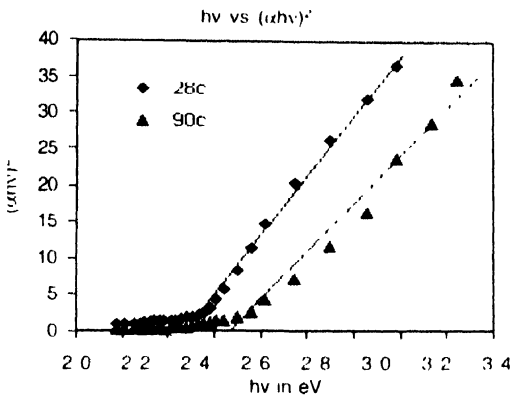

Figure 4(b). Band gap determination for precipitates at temp 28°C & 90°C

3.4. PL spectra :

It has been reported that, in case of CdS nanoparticles (NP's) embedded in polymers, the peak position of the surface defect PL emission of CdS NP's is weakly related to the size of the NP's[11]. However, PL spectra is more dependent on the surface states of the nanoparticles.

A room temperature PL spectra of two representative films deposited at solution temperatures 28°C and 90°C are shown in figure 5. At 28°C, the maximum PL peak at 520 nm is due to the band-to-band transition. However, at 90°C, the PL emission peak is more intense and shifted to the lower wavelength side at 436 nm. The other less intense broad peaks at 658 nm and 696 nm found in the long wavelength region is expected due to transitions at surface defect states [11,12,13,14]. Moreover, the intensities of both the PL peaks are found to increase when deposition temperature of the films are increased.

In case of precipitates, the less intense PL peak at 376 nm may be due to excitonic emission because of quantum confinement [15]. The excitonic energy is calculated to be 3.3 eV. The other intense sharp peak at 603 nm, clearly shows red shift because of the surface states of CdS nanoparticles. The defect level calculated to be 2.05 eV is a deep state preferably arises from sulphur vacancies. Further studies on this precipitates (powder samples) are in progress.

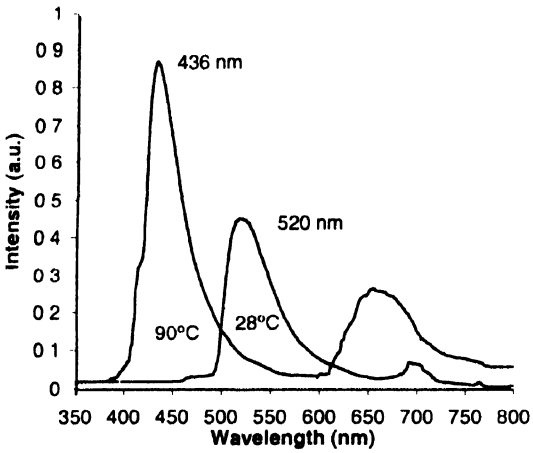

Figure 5(a). Photoluminescense spectra for films at temp 28°C and 90°C.

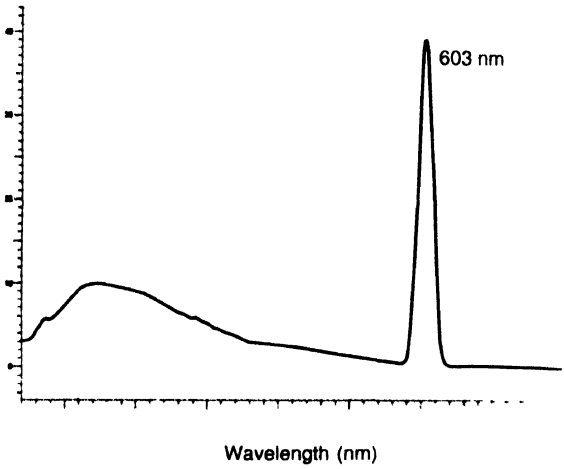

Figure 5(b). Photoluminescense spectra for precipitates at temp. 28°C and 90°C

4. Conclusion

Thin films as well as precipitates of CdS prepared by CBD technique in PVA matrix are found to be nanocrystalline. The crystallite sizes are found to be within 7 – 15 nm. The UV absorption of films at higher temperatures clearly shows an increase in band gap which supports the formation of nanocrystallites. It, therefore, shows that the films prepared at elevated temperatures of the solution exhibited strong quantum confinement effect as the optical band gap increases significantly, from 2.48 – 2.75 eV compared to bulk value 2.42 eV. Enhancement of PL intensity is also observed for the films prepared at higher solution temperatures. In case of precipitates, the PL emission spectra are dominated by surface defect level rather than band to band transitions.

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